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COMPLETE SPECIFICATION

Plasticised Linear Aromatic Polyester Compositions

We, THE GOODYEAR TIRE & RUBBER COMPANY, a corporation organized under the Laws of the State of Ohio, United States of America, with offices at 1144, East Market Street, Akron, Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to plasticized linear aromatic polyesters.

The linear aromatic polyesters in the solid state at room temperature are normally hard, tough materials. Because of their hardness and general inflexibility these polyesters are considerably limited in their applications and find their chief utility in thin films or fibers where in their inherent hardness and inflexibility are compensated for by the thinness of the pellicles or fibers. The addition of plasticizers to crystallizable polymers increases their rate of crystallization, and it has been found that many of the materials that are commonly used as plasticizers for polymers such as the vinyl resins increase the rate of crystallization of the linear aromatic polyesters to such an extent that they cannot be incorporated into the crystalline polyesters. An extremely rapid rate of crystallization is undesirable because usually the polymer must be worked or stretched or cold-drawn while it is in the amorphous state in order to have the product acquire certain desired physical characteristics. In addition to affecting the rate of crystallization, many of the materials that are ordinarily used as plasticizers for other polymers are not compatible with linear aromatic polyester resins and when incorporated in such resins separate out leaving the resin in its original unplasticized state.

It is an object of this invention to provide improved linear aromatic polyester compositions. It is another object to provide novel plasticized linear aromatic polyester compositions. It is another object to provide polyester

compositions having improved flow and processing properties. Other objects will appear hereinafter as the description of this invention proceeds.

The plasticizers of the invention can be incorporated in the polyester by various means. For example, the plasticizer can be added to a solution of the polymer in a suitable solvent, and the solvent can then be evaporated leaving the polymer homogeneously mixed with the plasticizer. In the case of polyesters having a low melting point and a low crystallization rate the plasticizer can be incorporated into the polyester by mixing the materials in a Banbury internal mixer or on a two-roll mill. In the case of copolyesters having high melting points and rapid crystallization rates the plasticizer can be suitably incorporated in the polyester by heating the plasticizer and mixing it while hot with hot molten polyester, as described in our application No. 1683/56 (Serial No. 805,588).

The practice of the invention is illustrated by the following examples.

EXAMPLE 1.

Ten grams of a 60-40 w/w ethylene terephthalate-ethylene isophthalate copolymer were blended with 2.0 grams of ditetrahydrofurfuryl adipate by mixing in a test tube at 171° C. The resulting mixture was then passed through a small mill a number of times to assure uniform blending, and was then molded at 177° C. into a film. The molded film from this composition was clear and far more flexible than a control sample to which no plasticizer had been added.

EXAMPLE 2.

Ten grams of a 60-40 w/w ethylene terephthalate-ethylene isophthalate copolyester were plasticized with 2.0 grams of dibenzylsebacate in the manner described in Example 1. The molded film from this composition was far more flexible than the control sample.

The esters used as plasticizers in this invention are the diaralkyl ditetrahydrofurfuryl and monoaralkyl monotetrahydrofurfuryl

esters of aliphatic dicarboxylic acids. The aliphatic group of the dicarboxylic acid radical can be straight or branched chain. In addition, the plasticizers can contain various substituents such as chloro, bromo, nitro, hydroxy, aryl and aryloxy groups, and alkyl and alkoxy groups containing from one to four carbon atoms in the group. Representative examples of acids from which the esters of this invention can be prepared are oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, alpha, alpha'-diethyl adipic acid, and alpha-ethyl suberic acid. Representative examples of esters of that class of this invention are dibenzyl, oxalate, dibenzyl malonate, dibenzyl succinate, dibenzyl glutarate, dibenzyl adipate, dibenzyl pimelate, dibenzyl suberate, dibenzyl azelate, dibenzyl sebacate, dibenzyl-alpha, alpha'-diethyl adipate, dibenzyl-alpha-ethyl suberate, ditetrahydrofurfuryl oxalate, ditetrahydrofurfuryl malonate, ditetrahydrofurfuryl succinate, ditetrahydrofurfuryl glutarate, ditetrahydrofurfuryl adipate, ditetrahydrofurfuryl pimelate, ditetrahydrofurfuryl suberate, ditetrahydrofurfuryl azelate, ditetrahydrofurfuryl sebacate, ditetrahydrofurfuryl-alpha, alpha'-diethyl adipate, ditetrahydrofurfuryl-alpha-ethyl suberate, di(methylbenzyl) succinate, di(methylbenzyl) adipate, di(ethylbenzyl) succinate, di(methoxybenzyl) adipate, di(chlorobenzyl) succinate, di(chlorobenzyl) adipate, di(bromobenzyl) succinate, di(bromobenzyl) adipate, di(nitrobenzyl) succinate, di(nitrobenzyl) adipate, di(hydroxybenzyl) succinate, di(hydroxybenzyl) adipate, benzyl tetrahydrofurfuryl succinate and benzyl tetrahydrofurfuryl adipate. Mixtures of such esters can be used if desired.

The polyesters with which this invention is concerned are the high molecular weight linear aromatic polyesters. The term "high molecular weight polyesters" is used in this specification and the appended claims to mean those polyesters having an intrinsic viscosity of at least 0.4 when measured at 30.0° C. in a solvent composed of a 60-40 w/w mixture of phenol and tetrachloroethane. Intrinsic viscosity is used as a measure of the degree of polymerization of the polyester and can be calculated using the Billmeyer extrapolation equation:

$$[\eta] = 1/4 \frac{\eta_{sp}}{C} + 3/4 \frac{\log \eta_r}{C}$$

in which

$$\frac{\eta_{sp}}{C} \text{ as } \eta_{sp} \rightarrow 0$$

[η], intrinsic viscosity, is the limit

$$\eta_{sp} = (\eta_r - 1)$$

$$\eta_r = \frac{\text{viscosity of solution}}{\text{viscosity of solvent}}$$

and C is the concentration in grams of the polyester per 100 cc. of the solution.

The term "aromatic polyester" whenever employed in the specification and claims is intended to mean a polyester in which the recurring structural unit contains an aromatic nucleus. Examples of aromatic polyesters are the polyesters derived by the self-condensation of hydroxy acids such as para-(beta-hydroxyethoxy) benzoic acid, para-(hydroxymethyl) benzoic acid, and para-(beta-hydroxyethyl) benzoic acid. Further examples are polyesters derived from the condensation of dicarboxylic acids such as terephthalic acid, isophthalic acid, 1,4-diphenoxy benzene-4',4''-dicarboxylic acid, 1,4-bis-(phenoxymethyl)-benzene-4',4''-dicarboxylic acid, (phenoxymethyl)-benzene-4,4'-dicarboxylic acid, phenoxy benzene-4,4'-dicarboxylic acid and diphenoxy alkane dicarboxylic acids with glycols such as ethylene glycol, trimethylene glycol, tetramethylene glycol and hexamethylene glycol. Further examples are polyesters derived from dihydroxy aromatic compounds such as hydroquinone and a dicarboxylic acid. Suitable derivatives of the acids such as the amides, acid chlorides, and the esters such as the methyl, ethyl, propyl, butyl, amyl and phenyl ester can be used. Various copolyesters from these and similar reactants can also be used. The polyesters derived from terephthalic acid and isophthalic acid or ester-forming derivatives thereof with a glycol, and terephthalate-isophthalate copolyesters constitute a preferred class. The invention has particular utility in its application to polymeric ethylene terephthalate and ethylene terephthalate-isophthalate copolymers especially those copolymers in which the ethylene-terephthalate units comprise from 90 to 40% of the sum of the ethylene terephthalate and ethylene isophthalate units and the ethylene isophthalate units comprise correspondingly from 10 to 60 percent of said sum.

While the plasticizers may be incorporated into the linear aromatic polyester over a wide range of concentration, generally from 5 to 60% by weight of plasticizer, based on the polyester, is sufficient. The preferred range of plasticizer is from 10 to 40% by weight of the polyester.

The plasticized polyesters of this invention have many advantageous properties and can be used for coating or impregnating cloth, for molding applications such as housings for radios, clocks and cameras, and can also be used for molding phonograph records when the highly crystalline, rapidly crystallizable

polyesters are used. Plasticized compositions from the polyesters having slower rates of crystallization can be used for wire coatings, extruded or cast films, which are useful in various packaging applications. The films can also be used for such applications as shower curtains, raincoats, aprons and table covers. Filaments of various of these compositions can be used in brushes, textiles, filters and in insect screening.

WHAT WE CLAIM IS:—

1. A composition comprising a linear aromatic polyester plasticized with an ester selected from the group consisting of diaralkyl, ditetrahydrofurfuryl and monoaralkyl monotetrahydrofurfuryl esters of aliphatic dicarboxylic acids.

2. A composition according to Claim 1 in which from 5 to 60% by weight of the plasticizer based on the polyester is incorporated into the linear aromatic polyester.

3. A composition according to Claim 1 or 2 in which the linear aromatic polyester is a polyester of terephthalic acid and/or isophthalic acid.

4. A composition according to Claim 3 in which the linear aromatic polyester is polymeric ethylene terephthalate.

5. A composition according to any of Claims 1 to 3 in which the linear aromatic polyester is a copolyester of ethylene terephthalate and ethylene isophthalate in which the ethylene terephthalate units comprise from 90 to 40% of the sum of the ethylene terephthalate and ethylene isophthalate units.

6. A composition according to any of Claims 1 to 5 in which the ester is ditetrahydrofurfuryl succinate.

7. A composition according to any of Claims 1 to 5 in which the ester is ditetrahydrofurfuryl adipate.

8. A composition according to any of Claims 1 to 5 in which the ester is ditetrahydrofurfuryl sebacate.

9. A composition according to any of

Claims 1 to 5 in which the ester is dibenzyl adipate.

10. A composition according to any of Claims 1 to 5 in which the ester is dibenzyl sebacate.

11. A process for the preparation of a composition which includes the step of incorporating an ester selected from the group consisting of diaralkyl, ditetrahydrofurfuryl and monoaralkyl monotetrahydrofurfuryl esters of aliphatic dicarboxylic acids with a linear aromatic polyester.

12. A process according to Claim 11 in which the ester may be mixed with the linear aromatic polyester in a dry or molten state or through a solvent medium said solvent thereafter being evaporated.

13. A process according to Claim 12 in which the plasticizer is incorporated into the linear aromatic polyester from 5 to 60% by weight of the plasticizer based on the polyester.

14. A process according to Claim 12 or 13 in which the linear aromatic polyester is a polyester of terephthalic acid and/or isophthalic acid.

15. A process according to any of Claims 12 to 14 in which the linear aromatic polyester is polymeric ethylene terephthalate.

16. A process according to any of Claims 12 to 15 in which the linear aromatic polyester is a copolyester of ethylene terephthalate and ethylene isophthalate in which the ethylene terephthalate units comprise from 90 to 40% of the sum of the ethylene terephthalate and ethylene isophthalate.

17. A composition of plasticized linear aromatic polyesters substantially as claimed and described hereinbefore.

18. A process for the preparation of a new composition of plasticized linear aromatic polyesters substantially as set forth and described hereinbefore.

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